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Modeling of a Reactive Separation Process Using a Nonequilibrium Stage Model

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Abstract

A nonequilibrium model for simulation of homogeneous reactive distillation has been developed. Mass transfer accompanied by simultaneous chemical reaction is described by the Maxwell Stefan equations. Calculations were done for the process to produce ethyl acetate that has been treated extensively in literature. It was found that reactions could, under certain conditions, have a significant impact on component efficiencies, thus emphasizing the need for rate-based models for reactive distillation. By means of parametric sensitivity studies it is shown that the effects of operational and design parameters on column behavior can be very complicated. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive distillation, Nonequilibrium model, Efficiency, Design

Introduction

In recent years several models for reactive distillation processes have been published. Most of these works employ an equilibrium stage model. When using equilibrium models, the number of actual stages required for a separation is obtained by multiplying the theoretical number of stages by a stage efficiency. We do not know if this is common practice for reactive distillation design, but without a link to actual mass transfer processes, an equilibrium stage model is of limited value for design purposes.

The usual way of accounting for departures from equilibrium is through an efficiency and the most common definition for a stage efficiency is the vapor phase Murphree stage efficiency. For component *i* this is given by:

$$E_i^{MV} = \frac{y_{iL} - y_{iE}}{y_i^* - y_{iE}} \tag{1}$$

Here, y_{iE} is the vapor phase composition on the tray below, y_{iL} is the actual vapor phase composition on the tray under consideration, and y_i^* is the composition of a vapor phase that would be in equilibrium with the liquid bulk on the tray. The latter can be determined from a bubble point calculation.

In reactive distillation however, the liquid phase composition is subject to changes due not only to mass transfer, but also to the chemical reaction. Efficiencies range from minus infinity to plus infinity, which makes their use somewhat problematic. Rate-based models do not use efficiencies but model the mass transfer process directly thereby avoiding this problem.

An equally important reason for using a rate-based model is that in reactive distillation operations we invariably have to deal with multicomponent mixtures exhibiting large thermodynamic non-idealities. Furthermore, chemical reactions taking place in the homogeneous liquid phase could significantly influence interphase mass transfers. None of the available models for reactive distillation takes into account the coupling between chemical reaction and mass transfer. These models implicitly assume that the reaction occurs in the bulk liquid only and not in the mass transfer film. Further complications, which have hitherto not been properly addressed, are the interactions between diffusing species in multicomponent mixtures and the coupling between diffusion and chemical reaction.

For conventional distillation operations, rate based models have been around for quite a while; they have provided valuable new insights on the effect of multicomponent mass transfer in the distillation process.

The first work in the field of rate-based reactive distillation modeling was presented in 1979 by Sawistowski *et al.* (1979), who modeled a reactive distillation column for esterification of methanol and acetic acid to methyl acetate. An effective diffusivity model was used as the mass transfer model, along with irreversible kinetics for the reaction.

Zheng *et al* (1992) presented a rate-based model for the simulation of MTBE production on a heterogeneous catalyst. A similar model was developed by Sundmacher (1995), also for MTBE production. These models use the Maxwell - Stefan equations for description of vapor/liquid mass transfer. The heterogeneous reaction is implemented as being pseudo homogeneous, where mass transfer effects to and from the catalyst are lumped into a catalyst efficiency term.

In addition, some commercial flowsheeting programs allow for rate-based reactive distillation modeling. In these models, the direct interaction between mass transfer and reaction usually is not taken into account. This means that the reaction is assumed to occur only in the bulk liquid and not in the mass transfer film.

In the following section we will discuss a model that takes the above considerations into account. We will focus here on homogeneous systems. Heterogeneous systems will be treated in a later paper.

Nonequilibrium stage modeling

A schematic diagram of a nonequilibrium stage is shown in Figure 1. This stage may represent a tray in a trayed column or a section of packing in a packed column. For each phase, we have mass, component and energy balances along with mass transfer relations for interphase mass transfer. The reaction is assumed to take place in the liquid phase only.

Mass transfer

A film model and the Generalized Maxwell-Stefan (GMS) equations will describe Gas/liquid mass transfer. For a system of *c* components, there are *c-1* independent Maxwell - Stefan equations (Taylor and Krishna, 1993):

$$\frac{x_i}{RT}\left(\frac{\partial \mu_i}{\partial \eta}\right) - \sum_{l=1}^{c} \frac{x_i \tilde{N}_l - x_l \tilde{N}_i}{c_t^L \kappa_{i,l}^L a} = 0 \qquad (2)$$

In this case the GMS equation is formulated in terms of mass transfer rates $\tilde{N}$ (*mol/s*) and mass transfer coefficients $\kappa_{i,l}^L a$, x_i is the mole fraction of component *i*, *R* is the gas constant (*J/mol K*), *T* is the temperature, μ_i is the chemical potential, c_t is the total molar concentration in mol/m^3.

The concentration of the *c-th* component can be obtained from the summation equation.

$$\sum_{i=1}^{c} x_i - 1 = 0 \qquad (3)$$

In a reacting system, we have to take into account the reaction in the film as well. The reaction will cause a change in the component mass transfer rates through the mass transfer film. We therefore have the following relation:

$$\left(\frac{\partial \tilde{N}_{i,j}}{\partial \eta}\right) - a\delta^L \sum_{m=1}^{nr} \nu_{i,m} R_{m,j} = 0 \qquad (4)$$

where $R_{m,j}$ represents the reaction rate of reeaction *m* in the film on stage *j* (mol/m^3s). $\nu_{i,m}$ is the stoichiometric coefficient of component *i* in reaction *m*. The term $a\delta_l$ is the total volume of the liquid film.

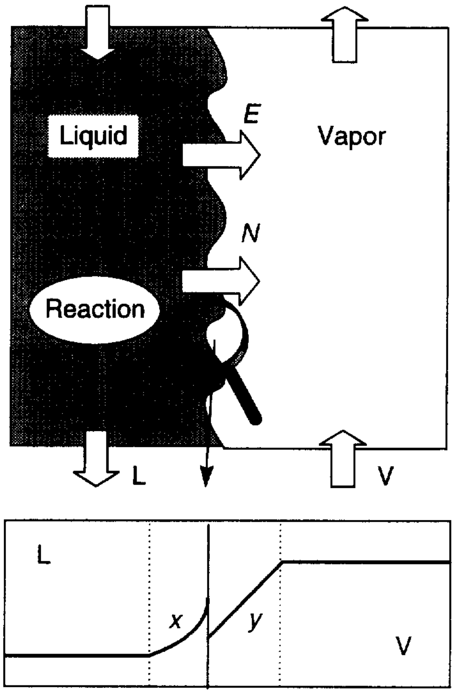

Figure 1: Schematic representation of a non-equilibrium stage

The fluxes are linked by the fact that the energy flux through the interface should be constant through the film. The above equations for the transfer films form a highly nonlinear set of linked differential equations, that cannot be solved analytically in general. We will, therefore, have to resort to numerical methods for solving the system. A finite difference method was used here. One should keep in mind that since equation (4) is a continuity equation, the finite difference equations should be written in conservative form.

Boundary conditions for the above system are provided by the mass, component, and energy balances over the control volume around the interface. At the interface we assume phase and thermal equilibrium. For each stage we have to solve for the variables presented in Table 1. The number of variables is given as well. Note that the mass transfer rates do not change in the vapor phase.

If we have *n1* discretisation points in the liquid film and *n2* discretisation points in the vapor film, this will lead to a total number of variables per stage of *6c + 6 + n1(2c+1) + n2(c+1)*. The reboiler and condenser are modeled as equilibrium stages. For these stages, we have to compute *2c + 4* variables: Liquid and vapor flow rate and composition, temperature and pressure.

Newton's method is used for solving the model equations. Details of the implementation and use of

Newton's method for solving a similar model are given by Taylor *et al.* (1994).

Liquid bulk		
	Flowrate	*1*
	Composition	*c*
	Mass transfer rates	*c*
	Temperature	*1*
Liquid film (for each discretisation point)		
	Composition	*c*
	Mass transfer rates	*c*
	Temperature	*1*
Interface		
	Liquid composition	*c*
	Vapor composition	*c*
	Mass transfer rates	*c*
	Temperature	*1*
Vapor film (for each discretisation point)		
	Composition	*c*
	Temperature	*1*
Vapor bulk		
	Flowrate	*1*
	Composition	*c*
	Temperature	*1*
Stage		
	Pressure	*1*

Table 1: Variables for each nonequilibrium stage

Design

Whereas in the equilibrium stage model a minimum of information is required with respect to column configuration (number of stages, feed location, reboiler and condenser type), a nonequilibrium stage model requires detailed knowledge of the column configuration, internals type and layout and so on. This is because a nonequilibrium stage model needs hydrodynamic information for the calculation of mass transfer and reaction rates. Values for the following parameters are required.

- V/L interfacial area
- Vapor and liquid mass transfer film thickness
- Total liquid holdup on a stage
- Mass and heat transfer coefficients for vapor and liquid phase
- Physical property data

These values cannot be chosen arbitrarily but depend directly or indirectly on primary variables such as flows, compositions and temperatures and on the column internals type. The column internals type is therefore required as an extra specification. Because of the direct link between hydrodynamic parameters and column behavior, column simulation and design should be done simultaneously.

Design problem

In specifying the internals type, we have two options: We can either specify the type, such as sieve trays, valve trays or packing, and let an automated design method take care of the details. This design can subsequently be used in the stage calculations. On the other hand we can design the trays beforehand and use the resulting tray layout as input for the model, as is typical for retrofitting. Both options are implemented in our model (see Kooijman, 1995).

The two most common design philosophies are to design to a specified Fraction of Flooding (FoF) and to a specified pressure drop (PD). The FoF method is commonly used for design of regular distillation trays. An initial design is based on some default values for the tray layout parameters such as weir height, hole diameters, hole pitch etc. In the design process these default values are modified based on a decision structure in such a way that eventually a tray is obtained which will operate at the desired fraction of flooding. The PD method usually is used for packings. Since we do not study packed columns in this paper we will not discuss this method.

The primary philosophies of these methods, and the decision structures are based on years of experience for normal distillation. There is nothing wrong with this in the sense that this way we will get a design that is hydrodynamically sound, but possibly far from optimal from an overall reactive distillation point of view. For example, the use of a higher weir height on a tray results in increased pressure drop but this is compensated for by a higher conversion in reactive distillation. For normal distillation operations, however, there may be no corresponding compensation for the increased pressure drop.

This is where a retrofit method is valuable. Once a design has been made with the grassroots mode, we can, modify parameters and evaluate the effect of changes. Furthermore we can check the influence of operational parameters such as reflux ratio and column pressure on an existing design. In this way ideas for the optimization of reactive distillation columns can be deduced.

A word of caution is in order, however: By choosing unusual column layouts we may move outside the range of reliability for (some of) the hydrodynamic equations. Within certain limits, however, this adjusting and retrofitting process will give us an indication on how a column is expected to behave as a result of changes in internals.

In the following section we will illustrate some of the above points with various calculations based on an example taken from the literature.

Example problem

The system under consideration here is the reactive distillation process for the production of ethyl acetate. Previous work on this system was done by, among others, Suzuki *et al.* (1971), Komatsu (1977), Komatsu and Holland (1977), Chang and Seader (1988) and Simandl and Svrcek (1991). Komatsu (1977) and Komatsu and Holland (1977) present a numerical and experimental study for a reactive distillation column

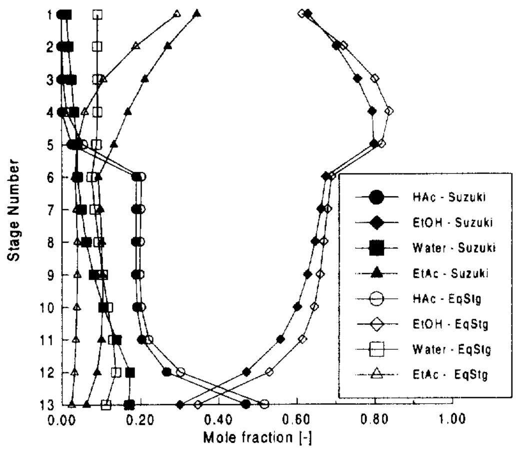

Figure 2: Concentration profiles as presented by Suzuki *et al.* (1971) and equilibrium stage model

with 7 stages and various feed stage locations. All other papers cited above present various numerical studies of a reactive distillation column with 13 stages.

The problem as presented by Suzuki *et al.* (1971) has been used as a test case for the program. Suzuki *et al.* perform calculations for a 13 stage column with a feed to stage 6. The column is operated at a reflux ratio of 10 and a bottoms flowrate of 0.8066 as a fraction of the feed. For further details, the reader is referred to Suzuki.

Calculations were done with an equilibrium stage model, similar to that presented by Simandl and Svrcek. (1991) and with the nonequilibrium stage model as discussed above. Wilson parameters were taken from Simandl. Results are presented in Figures 2-4. Shown in Figure 2 is a comparison between the calculated liquid phase concentration profiles, using the equilibrium stage model, and numerical data as presented by Suzuki. As can be seen, the differences are considerable, but the general trends in the concentration profiles are the same. This large difference is not a surprise, since different thermodynamic models were used.

Nonequilibrium stage model

For the calculations with the NEQ stage model, the feed rate was increased by a factor of 100. This was done to obtain internal flows for which the implemented hydrodynamic correlations can be used. In addition we neglected reactions that might be taking place in the reboiler and condenser. This because these stages are modeled as equilibrium stages, and they require the specification of a liquid volume for calculation of the reaction rate. At the time of writing we have not implemented correlations to tackle this problem.

Calculations were compared with calculations done with the equilibrium stage model. The nonequilibrium stage model was operated in grassroots mode, using the fraction-of-flooding method. Sieve trays were specified as column internals, with a desired flooding fraction of 0.75. Other specifications were the reflux ratio and the bottoms flowrate. The liquid volume, required as an extra input in the equilibrium stage model, was the average value from the calculated liquid volumes in the nonequilibrium stage model.

In Figure 3, a comparison is given between the liquid phase concentration profiles obtained by both models. Here, trends are similar as well, but there are differences caused by the influence of mass and heat transfer. The overall conversion based on ethanol found with the NEQ stage model is 34% as compared to 36% in the EQ stage model. One would normally expect the NEQ model to lead to a much lower conversion than the EQ model when the same number of stages (and reflux) are specified. It is indeed remarkable that the NEQ model results in only a marginally lower conversion than the EQ model. The explanation for this is given below by comparing the rates of production of ethyl acetate by the two models

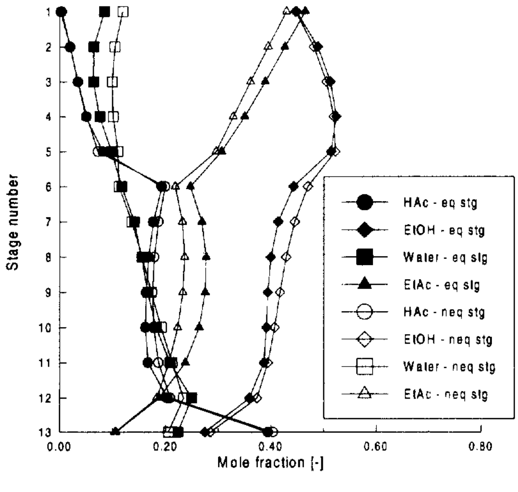

Figure 3: Comparison between equilibrium and non-equilibrium stage model

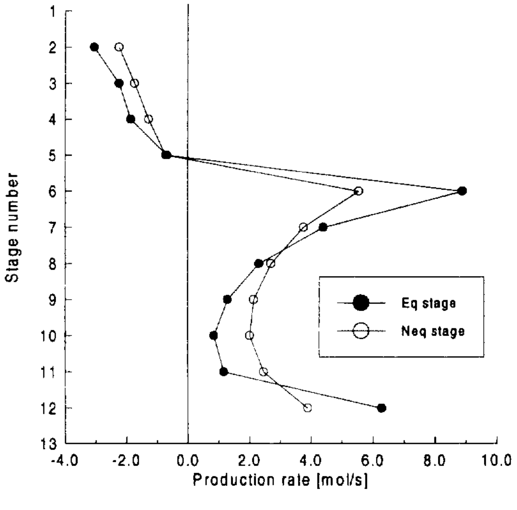

Figure 4: Comparison of production rates in equilibrium and nonequilibrium stage model

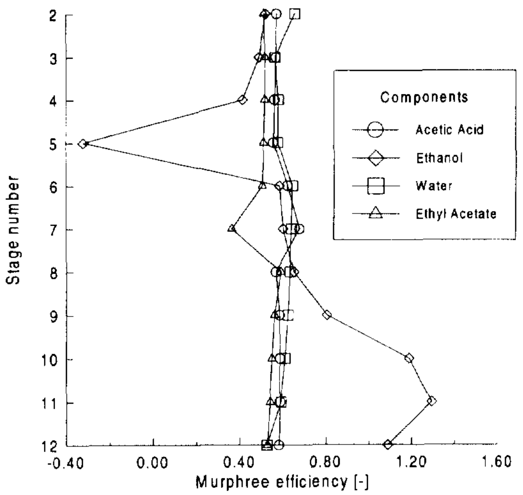

Figure 5 Murphree vapor phase efficiencies

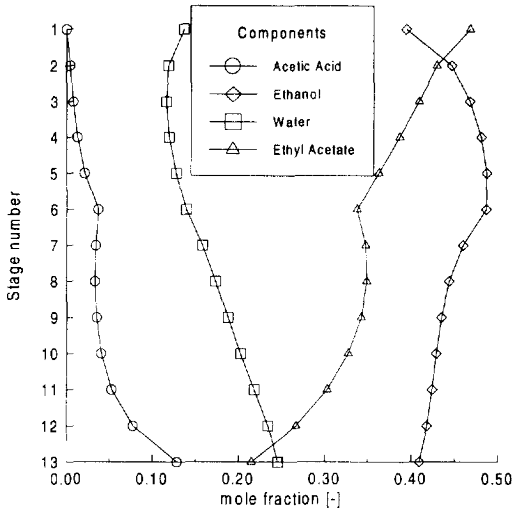

Figure 6: Vapor phase composition profiles, non-equilibrium stage model

(Figure 4). It is clear that the important part of the column with respect to EtAc production is the part below the feed. This is where we see high positive production rates. High production rates are found on the feed stage and on the last reactive stage of the column. Although in part of the bottom section, the production rate as found by the NEQ stage model is higher, the overall production rate (sum of stage production rates) is higher for the EQ stage model. The lower production rates in the equilibrium stage model indicate a composition that is closer to chemical equilibrium.

On the top trays negative production rates are found, which indicate consumption of EtAc. Chang and Seader (1988) reported similar behavior. What happens here is that the rectification of the product by means of the differences in boiling point is countered by a backward reaction.

It is interesting to observe that the consumption rate found with the equilibrium stage model is higher than with the nonequilibrium stage model. Introduction of mass transfer resistance (in the NEQ model) has the effect of preventing the reverse reaction to some extent. This emphasizes the importance of column design; If a column is too tall or has too much catalyst, the performance may be poorer than it could be. This places high demands on the predictive capability of reaction rates along the column, to ensure there is no overdesign.

Film reaction

Calculations were done to test the influence of the reaction in the mass transfer film. This was done by switching off the reaction in the mass transfer film and rerunning the calculations. No significant differences in the results were found. This is probably due to the fact that the reaction volume for the mass transfer film is negligible with respect to the liquid bulk volume. The total production in the film is therefore orders of magnitude smaller than the liquid bulk production.

One should keep in mind however that the system under consideration is reasonably well behaved: It is equistoichiometric it has a very low reaction enthalpy and concentration gradients in the transfer films are relatively flat. The effect of non-equistoichiometric reactions, or reactions with more pronounced thermal behavior still remains to be studied.

Efficiencies

With the concentration profiles calculated by the non-equilibrium stage model, we can now calculate the stage efficiencies for each component with equation 1. Results are shown in Figure 5. Given are the efficiencies for all components as a function of the stage number. We observe extrema in efficiencies for acetic acid and ethyl acetate at stage 7. For ethanol extrema are observed at stages 11 and 5 and for water at stage 3.

As can be seen from the vapor phase concentration profiles, given in Figure 6, all of these extrema, except one, coincide with a maximum or minimum in the vapor phase concentration profile along the column. It is only the maximum in ethanol at stage 11 that does not.

The other extrema in efficiencies can be explained by the following. First we will rewrite equation 1 in terms of differences in mole fractions:

$$E_i^{MV} = \frac{\Delta y_i}{\Delta y_i + \varepsilon_i} \tag{5}$$

with $\Delta y_i = y_{iL} - y_{iE}$ and $\varepsilon_i = y_i^* - y_{iL}$. At the inversion points the concentration differences over the

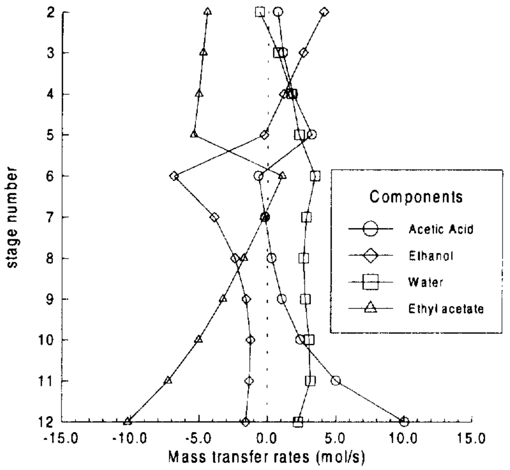

Figure 7: Mass transfer rates

trays are very small. In addition we have at these inversion points, almost by definition, a situation where the mass transfer rate for that specific component is very low. Shown in Figure 7 are the mass transfer rates of the various components as a function of the stage number. Mass transfer from the liquid to the vapor phase is considered to be negative. The very low mass transfer rates result in very low values of ε. In some cases, ε changes its sign, which will therefore result in a situation where the value of the denominator of equation (5) will be smaller than the numerator, leading to efficiencies greater than one. Generally speaking efficiencies are ill behaved at these inversion points, because of the small values for Δy and ε. It is therefore very hard to study the influence of the reaction at these points, since effects can not be separated in a good way. It is different for the maximum in the ethanol efficiency. Here there is no maximum in the ethanol concentration, as can be seen from the concentration profiles and from the mass transfer rates: The direction of mass transfer for ethanol stays the same over this section of the column. Unusual behavior based on the argument that ethanol is a trace component can be discarded as well: It is the main constituent of the mixture. The question then is how we can have efficiencies higher than one, while we are assuming ideally mixed flow in both phases.

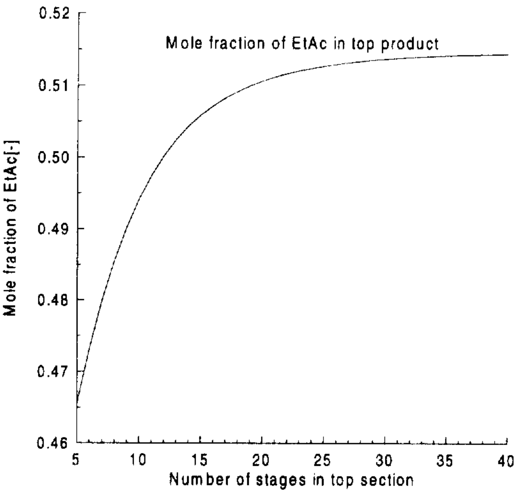

Figure 8: effect of the number of stages in the top section on top product purity

A possible reason for this is given by the following. Mass transfer occurs from liquid to vapor, which means that, if we would have no reaction:

$$\varepsilon = y_L^* - y_{iL} > 0 \qquad (6)$$

Because of the reaction however, we will have consumption of ethanol in the liquid phase, lowering the concentration of ethanol, which will lower the value of ε, possibly up to the point where ε becomes negative. This will then result in an efficiency that is greater than one. This is exactly what is observed.

The reason why we do not see this behavior for other components is that the concentration gradients along the column are much bigger in the areas of high reaction rates: the changes in ε are apparently negligible there.

The fact remains that reactions can severely affect efficiencies, especially in regions of low concentration gradients. This emphasizes the importance of rate based models.

Optimization

Suppose we want to increase the purity of ethyl acetate in the top stream of the base case column. From normal distillation we know that this can usually be accomplished either by adding stages, or by increasing the reflux ratio.

The effect of adding stages to the top section is presented in Figure 8. Given is the top product mole fraction of Ethyl Acetate. These calculations were done with the equilibrium stage model in order to save calculation time. We see that indeed a higher product purity is obtained if we increase the number of stages in the top section, but that after a certain number of stages, adding more stages does not result in a significant increase in product purity. Here we have reached a reactive azeotrope: Purification of the product, established by the equilibrium stage is countered by the backward reaction. Behavior of the column at this stage is similar to a nonreactive azeotrope. There is, however, one difference: The vapor and liquid phase compositions are not necessarily equal for a reactive azeotrope (Barbosa and Doherty, 1988).

Better results may be achieved if non-reactive stages are added to the top section or if some of the reactive stages in the top section are replaced by non-reactive stages. With this the effect of the backward reaction is cancelled in the rectification process. As a consequence, the reactive azeotrope may also disappear. Results of such simulations will be published in a follow-up paper.

The effect of the reflux ratio must be studied with the nonequilibrium stage model. This is, because a change in flows will result in different liquid holdups and interfacial areas; these directly influence column behavior. This interaction is more correctly accounted for in the nonequilibrium model. In the equilibrium stage model volumes must be specified. Here we use a column with the same layout as the base case column (at RR = 10). Operational limits are found at a reflux ratio of 14 (flooding) and a reflux ratio of 7 (excessive weeping).

Shown in Figure 9 are the top product mole fractions of EtAc as a function of the reflux ratio. It can be seen here, that the reflux ratio has no substantial influence on the mole fraction of EtAc in the product stream. Differences are within 0.4 mole fraction %. The reason for this probably lies in the fact that because of the higher reflux ratio, the stage compositions will be closer to chemical equilibrium, and the overall reaction rate will be lower. The higher reflux ratio also results in an increase in liquid holdup and, therefore, in an increase of reaction volume. The net production rate, which is a product of the reaction rate and the liquid volume will, therefore, not change substantially.

From above observations we can conclude that column optimization is not a straightforward problem. Changes in operational parameters influence the process at multiple levels due to the reaction. The combined effects are very hard to predict.

Internals Design

The liquid holdup has proven to be a very important factor in the reactive distillation process. Some calculations were, therefore, done to check the influence of the weir height on the performance of the process. These calculations were done with the tray layout obtained for the base case column. Weir heights were varied from 1 to 4 inches, over the entire column. An additional calculation was done for the case where in the bottom section a weir height of 4 inch was specified whereas in the top section a 1 inch weir was used. This is because in the bottom section the reaction rate is positive and we need large liquid volumes to get the biggest benefit out of this positive reaction rate, and in the top section we need small volumes in order to avoid consumption of the produced ethyl acetate.

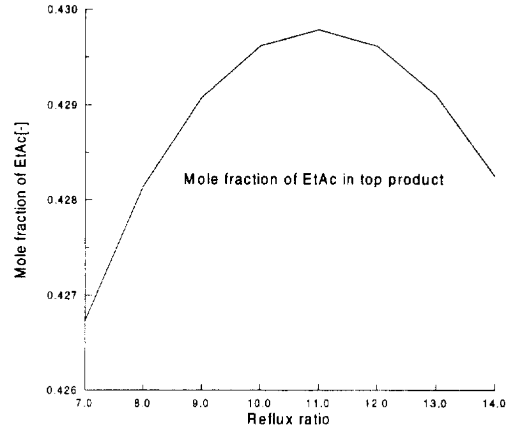

Figure 9: Effect of reflux ratio on top product purity

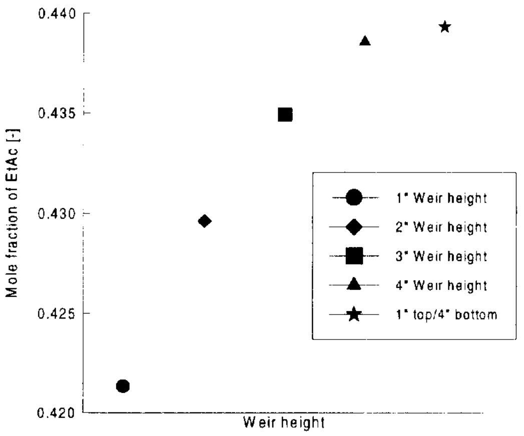

Figure 10: Concentration of EtAc in top product stream as a function of weir height

Figure 10 shows the top product content of ethyl acetate as a function of the weir height. Reaction rates along the column are given in Figure 11.

We see that with an increase in weir height, the top product purity increases. This can be understood if we look at the production rates of ethyl acetate (Figure 11). We see that a higher weir height results in a higher reaction rate, except in part of the bottom section of the column. In this section, the liquid phase composition is close to equilibrium and reaction rates are low: Since the reaction will be closer to equilibrium for a high liquid volume, we see here lower reaction rates for higher weir heights. However on the important stages, we see an increased production. The same holds for the top section: The higher the liquid volume, the higher

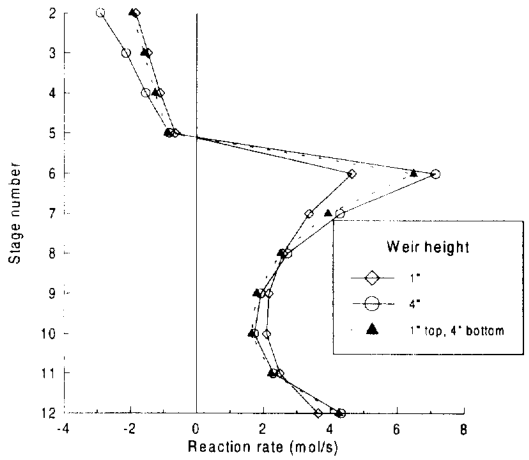

Figure 11: Production rates for various weir heights

the (backward) reaction rate. This is why it is interesting to look at methods for reducing the reaction rate on the top stages: Here, product is consumed and we would like to avoid that. Decreasing the weir height in the top section seems a possible way to do that. Results can be seen in Figures 10 and Figure 11 (dashed line) as well. The reaction rate in the top section of the column has indeed decreased, but so has the reaction rate in the bottom half of the column, in this case because of the changed concentration profiles. As can be seen, the net effect is only a minor increase in ethyl acetate content. Once again the importance of a good design is shown.

Conclusion

A rate-based model has been developed for calculation of reactive distillation processes. Calculations were done for a 13-stage column for the production of ethyl acetate from ethanol and water (Suzuki *et al.* 1971).

It was shown that efficiencies in the reactive distillation process could, under certain conditions, be affected by the reaction. The use of efficiencies in reactive distillation should, therefore, be avoided.

In addition calculations were done to test the influence of process and design parameters on the reactive distillation process. It was found that a change in one single parameter causes many changes throughout the column, which makes it almost impossible to make generalized predictions about column behavior. The importance of a good design is shown here as well: Slight overdesigns could easily lead to poorer column performance.

A rule of thumb in process engineering that a good design, even when operated badly is better than a bad design that is operated at its limits, holds even more strongly for reactive distillation, since the design can have a considerable impact on the process. Good models will be immensely valuable in this case since they allow for cheap and easy feasibility and optimization studies, without making too many simplifications.

This also emphasizes the need for research in areas of 'unconventional' tray designs and hydrodynamics. By limiting ourselves to conventional internals we might very well not get the most out of a column. Here we see a key role and need for good models as well. They can be a valuable help in determining the most important factors for reactive distillation optimization.

Acknowledgment

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Notation

a	Vapor/liquid interfacial area	m^2/m^3
c	Number of components	-
c_t	Total concentration	mol/m^3
E	Energy flux	W/m^2
E^{MV}	Murphree vapor phase efficiency	-
$\tilde{N}$	Mass transfer rate	mol/s
nr	Number of reactions	-
$n1$	Number of discretisation points liquid phase	-
$n2$	Number of discretisation points vapor phase	-
R	Gas constant	$J/(mol\ K)$
$R_{m,j}$	Reaction rate of reaction m	$mol/(m^3\ s)$
T	Temperature	K
x_i	Liquid mole fraction of species *i*	-
y_i	Vapor mole fraction of species *i*	-

Greek

δ	Mass transfer film thickness	m
ε	Mole fraction difference (see eq.(6))	-
η	Dimensionless film coordinate	-
κ	Binary mass transfer coefficient	m/s
μ	chemical potential	J/mol
ν	stoichiometric coefficient	-

subscripts

i	Component index
j	Stage number
l	Component index in summation
L	Referring to the liquid phase
m	Reaction index
t	Indicating total

superscripts

L	Indicating liquid phase property
M	Referring to Murphree
V	Referring to vapor phase

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